

Inhibited Counterflow Non-Premixed Flames with Variable Stoichiometric Mixture Fractions

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Introduction

The opposed-jet burner configuration has been used extensively to evaluate the performance of flame inhibitors¹⁻⁷. In this configuration the method of inhibitor addition and reactant composition can have a pronounced effect on the observed inhibitor effectiveness. The goal of this work is to investigate, experimentally, the influence of oxidizer-side versus fuel-side inhibitor addition at different stoichiometric mixture fractions.

Several researchers have investigated fuel-side and oxidizer-side addition of inhibiting agents, both numerically⁶, and experimentally⁷. The results indicate that the inhibitor effectiveness is a strong function of the side to which the dopant is added, and of the flame location, relative to the stagnation plane⁶⁻⁷. This can primarily be attributed to differences in the quantity of inhibitor that reaches the flame. Because the local gas composition at the stoichiometric contour, where the flame is assumed to be, is composed of contributions from both of the reactant streams, the dopant concentration there is less than that in the doped reactant stream alone. The results presented herein are the first experimental work, to our knowledge, which systematically maps inhibition effectiveness against the stoichiometric mixture fraction, a parameter that represents the relative contributions of the two streams at the stoichiometric contour.

Another significant contrast between the oxidizer-side and fuel-side doping arises from the nature of the inhibition mechanism. It has been hypothesized that the effectiveness of compounds which act chemically as well as physically to inhibit the flame, may depend in a more fundamental manner on which side the inhibitor is added⁸. Some of these inhibiting compounds are thought to catalytically promote radical recombination, in particular $H + OH \rightarrow H_2O$ and $H + H \rightarrow H_2$. Because most of the radical chemistry that is important for combustion reactions takes place on the oxidizer side of the flame⁸, it is proposed that, for a given concentration, inhibitor effectiveness will be higher for oxidizer-side addition than for fuel-side⁸. To investigate this hypothesis, both chemically-active and inert dopants were employed during this investigation. The inhibitory properties of the chemically active agent, dimethyl methylphosphonate (DMMP) $[P(=O)(CH_3)(OCH_3)_2]$, have been demonstrated previously using an opposed-jet burner apparatus⁹. Argon was used as the inert inhibitor.

Stoichiometric mixture fractions considered in this investigation ranged from 0.0544 (undiluted methane-air) with the flame on the oxidizer side of the stagnation plane, to 0.7 with the flame on the fuel side. For all conditions under consideration, extinction measurements were performed with fuel-side and oxidizer-side addition of both inert and chemically-active dopants. Results are presented in terms of reduction in the global extinction strain rate, normalized to the global extinction strain rate for the undoped cases.

Experimental

Experiments were conducted on an opposed-jet burner. Methane diluted with nitrogen was used as the fuel and a mixture of oxygen and nitrogen as the oxidizer. Variable dilution with nitrogen of both reactants allows for non-premixed flames to be stabilized on either the oxidizer or fuel side of the stagnation plane. The burner was aligned vertically with the lower tube used as the fuel source and the upper tube as the oxidizer source. A few experiments, conducted with the reverse orientation to study the effect of buoyancy, found no significant change in extinction strain rate. The burner was constructed from glass tubes 30 cm long with an ID of 0.98 cm, and a separation distance of 0.95 cm between opposing nozzles. Annular sheath flows of nitrogen are provided through 2.22 cm ID glass tubes. The sheath tube exits were offset by approximately 1 cm, upstream of the reactant tube exits, to minimize the impact of the sheath flow on the development of the reactant flows. The entire burner is isolated in a glass enclosure for control of exhaust gases. This enclosure is purged with nitrogen and maintained slightly below atmospheric pressure.

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The chemically-active flame inhibitor used during this investigation, DMMP, is a liquid at room temperature with a low vapor pressure (less than one torr at ambient temperature). In order to maintain sufficient concentrations of DMMP in the vapor phase, the reactant lines were heated to approximately 100°C with electrical heating tapes. The temperature of the reactant streams 10 cm upstream from the exit of the nozzles was maintained at 100±1°C via active control of the sheath flow. For all tests of chemically-inhibited flames, a constant loading of inhibitor of 500 ppm of DMMP was added to one of the reactant stream. Previous experiments have shown a 40% reduction in the global strain rate required to extinguish a non-premixed methane-air flame when the oxidizer stream was doped with 1500ppm of DMMP. Inert-additive testing was conducted with a loading of 25000 ppm of argon. The significant disparity in dopant concentrations between the inert and chemically-active cases is required due to the strong inhibitory effect of DMMP.

Results

Experiments were performed for a range of stoichiometric mixture fractions, Z_{st} , where Z_{st} can be evaluated from reactant compositions in the nozzles and the stoichiometry of the overall combustion reaction, using equation 1:

$$Z_{st} = \frac{Y_{O,-\infty}}{\left(\left(\frac{MW_O v_O}{MW_F v_F} \right) Y_{F,+\infty} + Y_{O,-\infty} \right)} \quad (1)$$

In this equation, Y is mass fraction, MW is molecular weight, v is the stoichiometric coefficient for complete combustion, the subscripts O and F refer to oxygen and fuel respectively, and the subscripts $\pm\infty$ refers to conditions at the fuel and oxidizer nozzles. Changing Z_{st} by varying the dilution of the oxidizer and fuel streams, moves the location of the stoichiometric contour, and thus the flame, relative to the stagnation plane. An undiluted methane-air flame has a $Z_{st} = 0.0544$. As Z_{st} is increased the stoichiometric contour moves closer to the stagnation plane until $Z_{st} = 0.50$. At this point the flame lies approximately at the stagnation plane, and for $Z_{st} > 0.5$ the flame lies on the fuel side.

There are two common methods for determining the extinction strain rate in flame measurements: direct measurement of the local strain rate using techniques such as Laser Doppler Velocimetry (LDV), or estimation of the strain from global parameters. For our experiments, the extinction strain rate was estimated using the latter method and will be referred to as the global strain rate, a_q . We use the following relation, proposed by Seshadri and Williams¹⁰, for evaluating the global strain rate:

$$a_q = \frac{2V_O}{L} \left(1 + \frac{V_F \sqrt{\rho_F}}{V_O \sqrt{\rho_O}} \right) \quad (2)$$

L refers to the separation distance between the nozzles, V is the stream velocity and ρ is the stream density. Equation 2 evaluates the strain rate in the oxidizer stream, at the stagnation plane for a non-reactive flow with a plug flow boundary condition at the nozzle exit plane.

For each value of Z_{st} , extinction measurements were performed for an undoped flame, a flame with dopant added to the oxidizer stream and a third case with the dopant added to the fuel stream. Global extinction strain for the doped cases were normalized by those of the undoped cases under the same conditions. Since the value of Z_{st} depends on two independent variables, Y_F and Y_O , fixing Z_{st} leaves one degree of freedom on reactant concentrations. Unique conditions were established by choosing the mass fraction of oxygen to give nominally equal undoped global extinction strain rates for each value of Z_{st} .

Figure 1 shows a plot of inhibition effectiveness for the inert inhibitor, argon. Each data point is the average of a minimum of 10 extinction measurements, the error bars indicate the minimum and maximum values observed. If the only important consideration for the inhibition effectiveness was the concentration of dopant at the flame and diffusivities of all important species were equal, then the oxidizer-side doping and fuel-side doping curves in figure 1 ought to intersect close to $Z_{st} = 0.5$. At this point the local gas composition at the flame contains an equal contribution from the fuel and oxidizer stream, thus the local dopant concentration would be the same no matter which stream is doped. The implications of unequal reactant and dopant diffusivities have not yet been explored quantitatively.

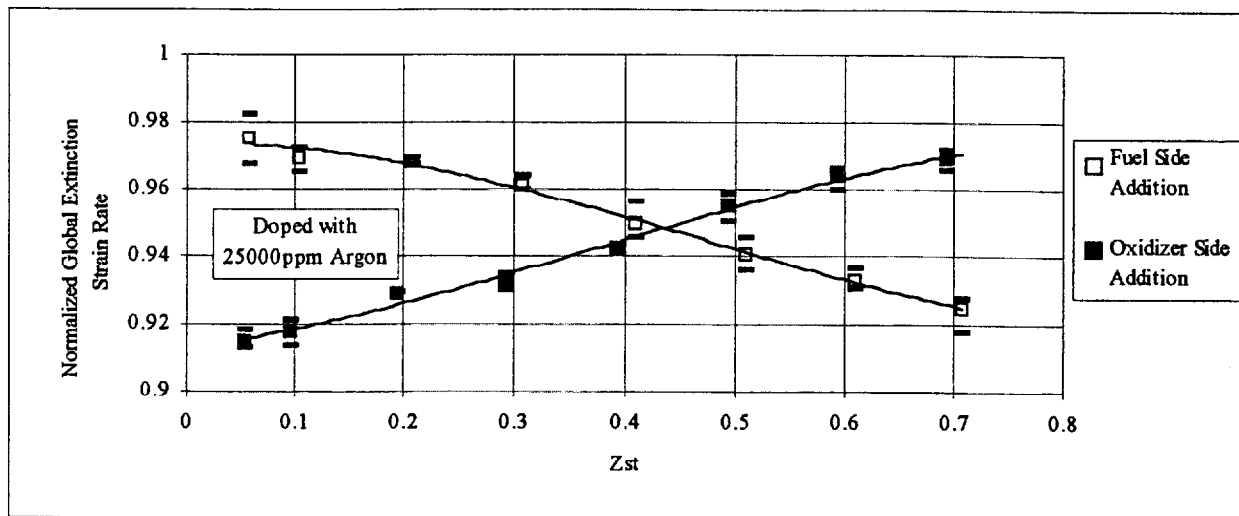


Figure 1. Variation of inert inhibitor effectiveness with stoichiometric mixture fraction. Fuel or oxidizer reactant streams doped with 25000 ppm of argon. Global extinction strain rates normalized to undoped value.

Figure 2 shows a plot of DMMP effectiveness for all cases considered. There was somewhat more scatter observed in the extinction measurements for DMMP doped flames than was observed with the inert dopant. Data points in figure 2 are the average of a minimum of 20 extinction measurements, performed over several days. It is interesting that the two curves in figure 2 do not intersect at $Z_{st} = 0.5$, but rather the intersection appears to be closer to $Z_{st} \approx 0.6$. This is significantly different from the result found with the inert dopant tests, $Z_{st} \approx 0.45$. The point of intersection has been shifted to the right, i.e. to a higher value of Z_{st} .

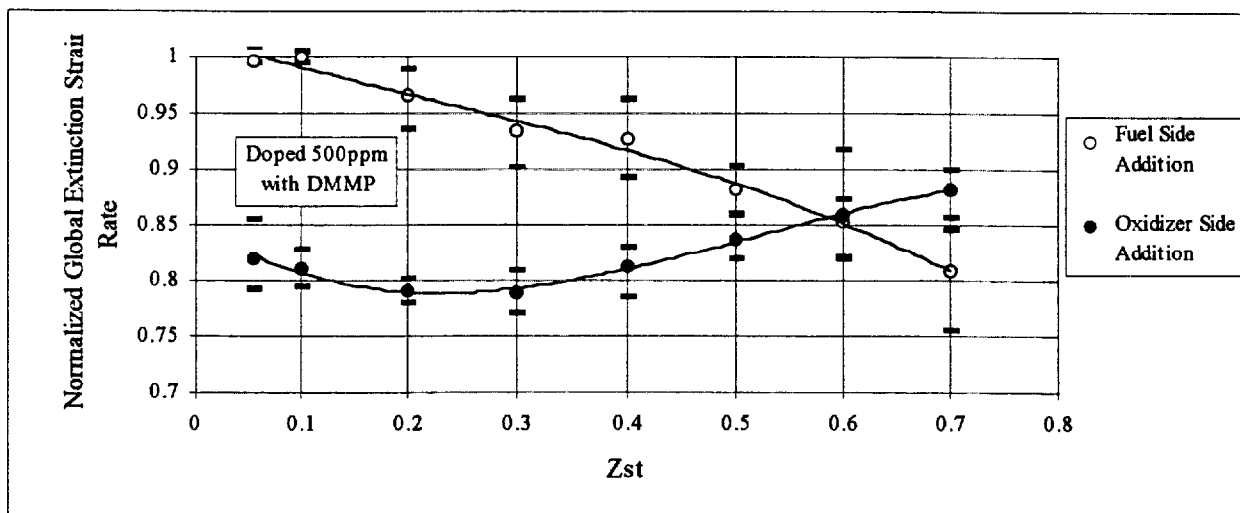


Figure 2. Variation of chemically-active inhibitor effectiveness with stoichiometric mixture fraction. Fuel or oxidizer reactant streams doped with 500 ppm of DMMP. Global extinction strain rates normalized to undoped value.

It is hypothesized that this shift can be attributed in part to the nature of the inhibition mechanism. Argon acts to inhibit the flame through purely physical means, via dilution and thermal capacity. The only important parameter affecting argon inhibition effectiveness is the quantity present at the flame. For DMMP, which acts primarily chemically, there are other considerations besides quantity. It is thought¹¹⁻¹³ that phosphorus-containing radicals, such as HOPO and HOPO₂ (formed from DMMP, and other phosphorus-containing compounds, during combustion) catalytically recombine the important combustion radicals, H and OH, slowing the overall reaction rate and thus inhibiting the flame. Several mechanisms for the catalytic cycle resulting in $H + OH \rightarrow H_2O$ and $H + H \rightarrow H_2$, have been suggested¹¹⁻¹³. With most of the important radical chemistry thought to be occurring on the oxidizer side of the flame⁸, it follows that agents, such as DMMP, which act via radical recombination ought to be more effective when introduced on that side. In accordance with

this hypothesis, the entire oxidizer-side addition curve would be shifted down relative to the fuel side addition curve. This is consistent with the observed increase in the value of Z_{st} at which the oxidizer-side and fuel-side curves intersect for the chemically-active flame inhibitor. Differences in the diffusivities of the inert and chemically-active dopants will also affect the location of intersection, but the change is not expected to be significant.

Summary

Experiments were performed to evaluate the effectiveness of inert and chemically-active flame-inhibitors when introduced from the oxidizer-side or the fuel-side of the flame. The stoichiometric mixture fraction, Z_{st} , was varied to change the relative position of the flame and stagnation plane, thus affecting the percentage of dopant that ultimately reaches the flame. Results indicate that the value of Z_{st} has a strong influence on the inhibitor effectiveness for both oxidizer- and fuel-side addition cases. A comparison of inert and chemically-active dopant results supports the hypothesis that chemically-active dopants are more effective when introduced from the oxidizer-side of the flame.

Acknowledgments

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